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(54) **Manufacture of rubber-modified co-polymers in an extruder-type reactor.**

(57) A process for producing resin comprising the reaction product of a rubbery polymer with one or more ethylenically-unsaturated monomers comprising the steps of:

(a) introducing a mixture of the rubbery polymer and one or more ethylenically-unsaturated monomers into a feed section of a screw extruder;

(b) polymerizing the monomers with the rubbery polymer in one or more additional reaction sections of the extruder, each section containing means to remove the heat of reaction to control the temperature therein;

(c) extruding the co-polymer formed at its melt temperature through a die head to produce the resin.

The product has an unexpectedly high impact resistance. In a representative example, the rubbery polymer is acrylonitrile/butadiene and the monomers are made up of a mixture of acrylonitrile and methyl acrylate.

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## TITLE

Manufacture of Rubber-Modified  
Co-Polymers in an Extruder-Type  
Reactor  
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This invention relates to the manufacture of rubber-modified co-polymers in an extruder-type reactor.

Rubber-modified resin have been produced by batch type reactions, typically those known as emulsion  
5 reactions. For example, U.S. Patent No. 3,821,348 discloses a resin produced by polymerizing a major portion of a mono-unsaturated nitrile such as acrylonitrile, a minor portion of another monovinyl monomer component and a preformed diene rubber.  
10 This batch reaction typically takes 4-5 hours to achieve a 90% conversion of monomer.

The polymerization of ethylenically-unsaturated monomers by themselves, in a screw extruder, is taught in U.S. Patent No. 3,536,680. However, the feeding  
15 of the rubbery polymer in addition to the monomers disclosed in this reference is novel. Screw extruders operate at a much higher temperature than emulsion processes. Such high temperatures normally will cause undesirable properties in rubber-modified

resins. Further, one would expect undesirable side reactions, for instance cross-linking, to occur because of these temperatures. Finally, since the rates of reaction for polymerizing a monomer is different from the rates of reaction for grafting the rubbery polymer onto the polymers being formed, one would expect the much shorter resident time in a screw extruder to adversely affect the properties of any resins formed.

10           An example of a method to avoid these problems caused by high temperature is found in U.S. Patent No. 3,133,135. This reference discloses very limited polymerization between an organic polymer such as butadiene-acrylonitrile rubber and acrylonitrile  
15           monomer using a spinaret. It is required that temperatures of this reaction be from about  $-80^{\circ}\text{C}$  to about  $90^{\circ}\text{C}$ . As noted in this reference, the final resin is formed immediately during the shaping of an article. Further, the amount of conversion  
20           of monomer is extremely low.

Contrary to these teachings, it has been found that a resin containing a rubbery polymer that has high impact resistance may be formed in a screw extruder at high temperatures.

25           According to the invention there is provided a process for producing a resin comprising the reaction product of a rubbery polymer with one or more ethylenically unsaturated monomers comprising the steps of:

- 30           a) introducing a mixture of the rubbery polymer and one or more ethylenically unsaturated monomers into a feed section of a screw extruder;
- b) polymerizing the monomers with the rubbery polymer in one or more additional reaction section  
35           of the extruder, each section containing means to

remove the heat of reaction to control the temperature therein;

c) extruding the co-polymer formed at its melt temperature to produce the resin.

5 Both the monomers and the rubbery polymers are those well known in the art. Suitable ethylenically unsaturated monomers which can be polymerized with each other are, for instance, styrene, acrylonitrile, acrylic acid and methacrylic acid, the various esters  
10 of these acids such as methylacrylate, amides, etc. These monomers can be polymerized alone (with the additional rubbery polymer) or in admixture with other such monomers acrylonitrile and methacrylate represent preferred monomers.

15 Suitable rubbery polymers are for example, butadiene/acrylonitrile, butadiene/styrene, polybutadiene and ethylene-polymers-diene rubber. Of these polymers butadiene/acrylonitrile is preferred.

In producing the resins from these components,  
20 other items are added such as initiators, chain transfer agents, and additives such as dyes and stabilizers. The use and amount of such items, along with the amount of monomers and rubbery polymers are all known in the art and not the subject  
25 of the present invention.

Screw extruders are also well known in the art, as described in U.S. Patent No. 3,799,234. Specifically, the extruder of the present invention should contain a feed section followed by two or more  
30 reaction sections and a final extrusion port.

The feed section is simply a means of obtaining all of the reaction components in a well dispersed state prior to the screw increasing the pressure through the extruder. It is important that the monomers

be in a liquid state. This may be accomplished by regulating the temperature of the feed section and/or the pressure of the components being fed. The rubbery polymer may be added to the feed section  
5 by dispersing the polymer in one of the monomers, water or a solvent. It is preferred that the rubbery polymer be dispersed in one of the monomers to be reacted to minimize additional processing steps. For example, even if water is utilized, this water must  
10 be removed with an additional dewatering section of the extruder.

The extruder will operate at pressures of from 0.7 kg/cm<sup>2</sup> gauge (10 psig) or greater and temperatures from ambient up to the melt temperature of the final  
15 resin produced. This melt temperature can be in the neighbourhood of 350°C or greater.

After the feed section, there should be at least one or more reactor sections, preferably two or more. Each reactor section has means for removing  
20 the heat of reaction and thus controlling the temperature of this section independent of the other section. In this manner, a temperature gradient can be developed from the feed section up to the final temperature necessary for melt extrusion. This will  
25 allow control of the polymerization of the monomers. Such means are known in the art, and may consist, for example of cooling water flowing around the reaction section.

There may also be additional sections for de-  
30 watering or de-gassing the resin prior to final extrusion. Thus if complete conversion of the monomer is not achieved, the residual monomers can be removed in this section prior to forming the resin.

Finally, the last section of the extruder contains an extruder die for forming the resin into

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the final desired shape.

The following Example illustrates the invention:

EXAMPLE

5 An acrylonitrile-rubber resin was prepared in  
a Werner-Pfleiderer twin-screw extruder having a  
feed section, five independently controlled temperature sections, and a die head. The screw was  
operated at 75rpm. 27 grams/minute of a liquid  
solution of 75 parts acrylonitrile/25 parts methyl  
10 acrylate/one part mercaptan chain transfer agent was  
fed to the feed section of the screw extruder.  
Dissolved in this stream was 2.45 grams/minute of an  
acrylonitrile/butadiene rubber polymer. To the feed  
section was added 0.40 grams/minute of polymeriz-  
15 ation initiator. The feed section was at ambient  
temperature and 10.5 kg/cm<sup>2</sup> gauge (150 psig).  
Cooling water was used to control the temperature of  
the five additional reactor sections. The temperature  
were as follows:

20	Section 1	230°F (110°C)
	Section 2	250°F (121°C)
	Section 3	300°F (149°C)
	Section 4	320°F (160°C)
	Section 5	350°F (176°C)
25	Die head	350°F (176°C)

20.8 grams/minute of resin was produced with  
a total monomer conversion of 77%. The estimated  
residence time in the extruder was 4 minutes. The  
resin was then tested for notched Izod and found to  
have a value of 1.65 ft/lbs/inch. This is compared  
30 to resins made in the extruder not containing the  
rubbery polymer having a notched Izod of approxima-  
tely 0.11. A polymer is considered to have good  
impact resistance if the notched Izod has a value  
about 0.5. Thus the present invention contrary to

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the high temperatures, short resident time and different reaction rates of monomer-monomer versus monomer-polymer, has achieved an unexpectedly high value for impact resistance.

Claims:-

1. A process for preparing resin comprising the reaction product of a rubbery polymer with one or more ethylenically-unsaturated monomers comprising the steps of:

a) introducing a mixture of the rubbery polymer and one or more ethylenically-unsaturated monomers into a feed section of a screw extruder;

b) polymerizing the monomers with the rubbery polymer in one or more additional reaction sections of the extruder, each section containing means to remove the heat of reaction to control the temperature therein;

c) extruding the co-polymer formed at its melt temperature through a die head to produce the resin.

2. A process as claimed in claim 1 characterised in that the rubbery polymer is a butadiene/acrylonitrile, butadiene/styrene, polybutadiene or ethylene-propylene diene rubber.

3. A process as claimed in claim 1 characterised in that the polymer is butadiene/acrylonitrile.

4. A process as claimed in any of claims 1 to 3 characterised in that the ethylenically-unsaturated monomers are one or more of the following acrylonitrile, styrene, acrylic acid and methyl acrylate.

5. A process as claimed in any of claims 1 to 3 characterised in that the ethylenically-unsaturated



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monomers are acrylonitrile and/or methyl acrylate.

6. A process as claimed in any of claims 1 to 5 characterised in that the extruder contains a de-watering section between the reaction section and the die head.

7. A process as claimed in any of claims 1 to 6 characterised in that the extruder contains a de-gassing section between the reaction section and the die head.

8. A process as claimed in any of claims 1 to 7 characterised in that the extruder is a twin-screw extruder.

9. A process as claimed in any of claims 1 to 8 characterised in that the resin produced has a notched Izod of greater than 0.5.

10. A process as claimed in any of claims 1 to 9 in which the ethylenically unsaturated monomers are fed to the extruder in the liquid state.

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# EUROPEAN SEARCH REPORT

Application number

EP 80 30 3936

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p>US - A - 3 513 145 (J.R. CRAWFORD)</p> <p>* Claims 1,3; column 4, lines 29-37 *</p> <p>--</p>	<p>1,2,4, 7,8,10</p>	<p>C 08 F 279/02 255/02</p>
	<p>FR - A - 2 278 709 (SHELL)</p> <p>* Claims 1,5,6; page 3, lines 20-24 *</p> <p>-----</p>	<p>1,2,4, 10</p>	
			<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 3)</p>
			<p>C 08 F 279/00 279/02 255/02 255/06 291/02</p>
			<p>CATEGORY OF CITED DOCUMENTS</p>
			<p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p>
<p>X The present search report has been drawn up for all claims</p>			<p>&amp;: member of the same patent family, corresponding document</p>
<p>Place of search The Hague</p>		<p>Date of completion of the search 27-01-1981</p>	<p>Examiner PEETERS J.C.</p>

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**ABSTRACT:**

CHG DATE=19990617 STATUS=O> In apparatus for the reverse osmosis purification of water or other fluid in a module (10) containing a membrane (11), the water is forced into the module (10) under pressure using two or more piston-cylinder assemblies (25, 26) mechanically interconnected with the pressurised fluid from the module applied to the rear face of the piston (27 or 28) which, from its front face, is driving water into the module, a low pressure continuously operating pump (20) providing a low pressure on the other piston to supply the necessary extra pressure. Valve means (30, 31, 33, 34) automatically reverse the functions of the two cylinders at each end of each stroke. This arrangement obviates any need for a mechanical drive to the pistons of the piston-cylinder assemblies (25, 26).